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(51) International Patent Classification ⁶ : C10G 27/12, A01N 37/00	A1	(11) International Publication Number: WO 97/47708 (43) International Publication Date: 18 December 1997 (18.12.97)
(21) International Application Number: PCT/GB97/01537 (22) International Filing Date: 9 June 1997 (09.06.97) (30) Priority Data: 9612035.7 8 June 1996 (08.06.96) GB (71) Applicant (for all designated States except US): OILFIELD CHEMICAL ADDITIVES LTD. [GB/GB]; Craigshaw Road, West Tullos, Aberdeen AB1 3AP (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): BRANKLING, David [GB/GB]; 18 Corse Gardens, Kingswells, Aberdeen AB15 8TN (GB). (74) Agent: MURGITROYD & COMPANY; 373 Scotland Street, Glasgow G5 8QA (GB).		(81) Designated States: AU, AZ, BR, CA, CN, DE, DK, ES, GB, GE, KR, KZ, MX, NO, NZ, RU, TM, TR, UA, US, UZ, VN, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: METHOD OF INHIBITING RESERVOIR SOURING BY BACTERIA (57) Abstract A method of inhibiting the growth of bacteria, especially anaerobic sulphate reducing bacteria, within oil and gas reservoirs by the addition of peroxy compounds to injected flood water is described. Suitable peroxy compounds include one or more of methyl ethyl ketone peroxide, cyclohexanone peroxide, acetyl acetone peroxide, diacetone alcohol peroxide, dibenzoyl peroxide, ditertiary butyl peroxide, tertiary butyl peroxide, hydrogen peroxide, tertiary butyl peroxy benzoate, inorganic and organic peroxycarbonates, or functional equivalents or derivatives of these compounds. The peroxy compound additives have the advantage of being thermally sensitive such that penetration into the reservoir and placement in strategic zones can be achieved leading to sterilisation deep within the reservoir. The compounds may also be tailored to optionally scavenge hydrogen sulphide produced by bacterial growth from the reservoir fluids.		

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1 **METHOD OF INHIBITING RESERVOIR SOURING BY BACTERIA**

2

3 The present invention relates to a method of reducing
4 the souring of hydrocarbons due to bacterial production
5 of hydrogen sulphide gas.

6

7 During the production of hydrocarbon fluids, such as
8 oil or gas, it is common practice to flood the
9 reservoir holding the hydrocarbons with water to
10 enhance production by maintaining pressure as oil
11 and/or gas is removed and to "sweep" hydrocarbons which
12 would normally remain within the reservoir to the
13 collection well.

14

15 The source water used in such flooding operations is
16 frequently a natural brine and in the case of offshore
17 oil and gas production is normally sea water.

18

19 Flooding of a reservoir with natural brines usually has
20 undesirable consequences since the brine may be
21 responsible for the introduction and/or accelerated
22 growth of bacteria within a reservoir as follows:

23

- 24 1. Bacteria within the brine flood water are
25 introduced to the reservoir and find a hydrocarbon

1 source (for example, oil). The oil may then be
2 metabolised by the bacteria allowing the rapid
3 growth of bacterial populations.
4

5 2. Bacteria which may be naturally present in the
6 reservoir in dormant form will receive a nutrient
7 supply due to the introduction of the flood water.
8 Again, the increased nutrient supply will promote
9 bacterial growth within the reservoir.
10

11 Generally, anaerobic conditions will exist in the
12 reservoir, and bacteria able to cope with low amounts
13 of oxygen or the absence of oxygen will preferentially
14 proliferate. Generally, the most dominant form of
15 bacteria is the so called sulphate reducing bacteria
16 (SRBs). SRBs metabolise sulphates from the injected
17 flood water and produce hydrogen sulphide gas as a
18 waste product.
19

20 The hydrogen sulphide generated will become partitioned
21 in both the oil/gas and water phases within the
22 reservoir. More importantly, however, the hydrogen
23 sulphide would normally be co-produced in the fluids at
24 the producing well.
25

26 The process of hydrogen sulphide production by bacteria
27 is known as reservoir souring. The consequence of this
28 process is a gradual increase in hydrogen sulphide
29 content within the produced fluids.
30

31 Hydrogen sulphide is highly undesirable in the produced
32 fluids since it is corrosive and toxic. Consequently,
33 the presence of hydrogen sulphide as a contaminant
34 adversely affects the sales quality of the exported oil
35 and gas.
36

1 It is thus normal practice within the industry to
2 attempt to prevent bacterial growth within the
3 reservoir by the addition of biocides to the injected
4 water in order to sterilise the system and therefore
5 prevent proliferation of bacteria.

6
7 Typical biocides include chlorine, aldehydes such as
8 gluteraldehyde, thiazolines and quaternary amines.

9
10 However, the continual addition of biocide is
11 frequently too costly to practice and more usually a
12 sweep dosage at suitable intervals is used to sterilise
13 the system.

14
15 Despite biocide addition, it is almost impossible to
16 prevent the introduction of all bacteria to a reservoir
17 and a reduced rate of souring may still occur.

18
19 Additionally, due to the surface active nature of the
20 majority of biocides, the biocides are readily absorbed
21 to the surfaces of minerals such as clays found in
22 reservoir sands. It is therefore not normally possible
23 to achieve penetration of the biocide deep into a
24 reservoir.

25
26 Hence elimination of bacteria naturally present within
27 a reservoir or introduced by the flood water and moving
28 with oil/water flood front boundary is normally not
29 achievable using conventional biocides.

30
31 One way to obtain an end product having acceptably low
32 levels of hydrogen sulphide is the removal of that gas
33 by treating the extracted hydrocarbons. This will
34 normally require the installation of process equipment
35 to remove the hydrogen sulphide gas by, for example,
36 flaring, treating with amine scrubbers to absorb the

1 gas or addition of chemicals to scavenge by reaction to
2 produce a neutralised compound.

3
4 However, all such methods of hydrogen sulphide removal
5 considerably increase the cost of production and are
6 generally considered to be undesirable.

7
8 In summary, it can be seen that a number of options
9 exist to prevent build up of hydrogen sulphide in the
10 produced fluids:

- 11
- 12 a. inhibit the growth of bacteria within the
13 reservoir by chemical addition to the flood water;
14
 - 15 b. scavenge the evolved hydrogen sulphide within the
16 reservoir to prevent production with recovered
17 fluids.

18
19 However, as indicated above, it is apparent that such
20 treatments are not practical using conventional
21 biocides or scavengers from performance and/or cost
22 constraints.

23
24 We have now found that the use of peroxy compounds
25 (which are not normally thought of as biocides) are
26 ideally suited to the treatment of bacterially
27 contaminated reservoirs. The peroxy compounds can both
28 destroy resident bacteria and also act to remove
29 hydrogen sulphide already generated.

30
31 In one aspect, the present invention provides a method
32 of inhibiting the growth of bacteria in a hydrocarbon
33 reservoir, said method comprising introducing a peroxy
34 compound to said reservoir.

35
36 In another aspect, the present invention provides a

1 method of combatting the generation of hydrogen
2 sulphide in a hydrocarbon reservoir by sulphur reducing
3 bacteria, said method comprising introducing a peroxy
4 compound to said reservoir.

5

6 The complementary actions of the peroxy compounds arise
7 from the oxidising potential of such compounds and the
8 generation of free radicals as the peroxy compound
9 decomposes.

10

11 The peroxy compounds for use in the present invention
12 are normally stable neutral compounds which therefore
13 show minimal absorption to the reservoir minerals and
14 can therefore penetrate deep into the reservoir carried
15 by the flood water.

16

17 The peroxy compounds of interest may be selected to
18 decompose at the particular temperatures encountered
19 within the reservoir (usually elevated temperatures
20 relative to the ambient). Particular activation
21 temperatures can be engineered by selection and/or
22 modifications of the peroxy compounds used, to allow
23 the selective placement of compounds within reservoirs
24 of widely differing temperatures.

25

26 Decomposition of the peroxy compounds leads to the
27 generation of free radicals which are highly aggressive
28 towards living cells. The free radicals cause damage
29 and ultimately destroy cells such as bacteria.

30

31 In addition, the generation of coincident oxidising
32 species occurs and these oxidising species will react
33 with hydrogen sulphide leading ultimately to formation
34 of harmless sulphates in the produced fluids.

35

36 The peroxy compounds therefore have the advantages of

1 being selective to the destruction of bacteria without
2 being lost to the reservoir by absorption or
3 decomposition prior to deep penetration. The peroxy
4 compounds also remove encountered hydrogen sulphide to
5 prevent continued production within the recovered
6 fluids.

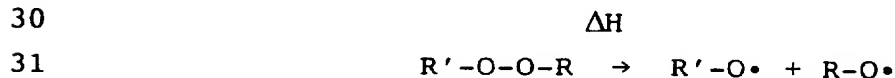
7
8 The type of peroxy compounds useful for this invention
9 contain the chemical grouping -O-O- and may be
10 generally described by the formula:



13
14 where R and R' may be hydrogen, alkyl or aromatic
15 groups (including substituted cyclic and branched
16 groups), oxygenated hydrocarbon chains such as
17 carbonate or ketone, or other groups which will result
18 in stabilisation of the peroxide linkage.

19
20 Modifications to the structure of R and R' alter the
21 solubility characteristics and thermal stabilities of
22 the peroxides which allows for selective placement and
23 activation in reservoirs of differing temperatures and
24 can also allow penetration of oil layers by selection
25 of oleophilic peroxides should this be desirable.

26
27 The reaction occurring by thermal decomposition of the
28 peroxy compounds leads to the generation of free
29 radicals, thus:

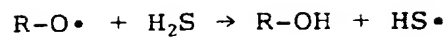


32
33 The generated free radicals may undergo various
34 reactions leading to complex organic products but all
35 such reactions lead to cellular attack and therefore
36 have biocidal properties.

1 In addition, the reaction:

2

3



4

5 can take place to give a reactive thiol free radical
6 ($\text{HS}\cdot$) which will bind to organic materials such as
7 crude oil or bacterial cells to eliminate free H_2S from
8 the system.

9

10 A further decomposition reaction can lead to the
11 formation of free oxygen which again limits bacterial
12 activity by altering the oxygen free conditions
13 necessary for SRB growth.

14

15 The described peroxy compounds therefore provide
16 advantageous multifunctional behaviour which can
17 prevent reservoir souring.

18

19 Viewed from a further aspect, the present invention
20 provides the use of a peroxy compound to inhibit
21 bacterial growth within a hydrocarbon reservoir or
22 to reduce the hydrogen sulphide content of a
23 hydrocarbon fluid.

24

25 In addition, the present invention also provides a
26 hydrocarbon fluid (eg oil or gas) containing a peroxy
27 compound or a reactant thereof as an additive.

28

29 The range of useful peroxy compounds to be applied to a
30 reservoir may be characterised by a self accelerating
31 decomposition temperature (SADT) where a critical value
32 will cause the compound to decompose at an accelerating
33 rate yielding the free radicals necessary for biocidal
34 activity.

35

36 However, the value may be adjusted by the inclusion of

1 accelerators or inhibitors which allow a peroxy
2 compound to be utilised at temperatures above or below
3 this figure.

4
5 Examples of suitable peroxy compounds which may be
6 added to a reservoir flood water for the purpose of the
7 invention include, but are not limited to:

8
9 Methyl ethyl ketone peroxide,
10 Cyclohexanone peroxide,
11 Acetyl acetone peroxide,
12 Diacetone alcohol peroxide,
13 Dibenzoyl peroxide,
14 Ditertiary butyl peroxide,
15 Tertiary butyl peroxide,
16 Hydrogen peroxide,
17 Tertiary butyl peroxy benzoate,
18 Inorganic and organic peroxycarbonates, or

19
20 functional equivalents or derivatives of these
21 compounds. A mixture of such compounds may be used.

22
23 Other compounds which are known to generate oxidative
24 free radicals by thermal or catalytic decomposition
25 will show similar biocidal activity.

26
27 Generally, the peroxy compounds will be added to the
28 flood water prior to injection into the reservoir.

1 CLAIMS

2

3 1. A method of inhibiting the growth of bacteria in a
4 hydrocarbon reservoir, said method comprising
5 introducing a peroxy compound to said reservoir.

6

7 2. A method of combatting the generation of hydrogen
8 sulphide in a hydrocarbon reservoir by sulphur
9 reducing bacteria, said method comprising
10 introducing a peroxy compound to said reservoir.

11

12 3. A method as claimed in either one of Claims 1 and
13 2, wherein the peroxy compound may consist of a
14 water soluble or water dispersable inorganic or
15 organic based peroxy compound.

16

17 4. A method as claimed in any one of Claims 1 to 3,
18 wherein the peroxy compound may be a peroxide,
19 hydroperoxide, peroxy carbonate, peroxy sulphate or
20 other peroxide based complex.

21

22 5. A method as claimed in any one of Claims 1 to 4,
23 wherein the peroxy compound may be selected from
24 one or more of methyl ethyl ketone peroxide,
25 cyclohexanone peroxide, acetyl acetone peroxide,
26 diacetone alcohol peroxide, dibenzoyl peroxide,
27 ditertiary butyl peroxide, tertiary butyl
28 peroxide, hydrogen peroxide, tertiary butyl peroxy
29 benzoate, inorganic and organic peroxy carbonates,
30 or functional equivalents or derivatives of these
31 compounds.

32

33 6. A method as claimed in any one of Claims 1 to 5,
34 wherein said peroxy compound is added to the
35 reservoir flood water.

36

- 1 7. A method as claimed in any one of Claims 1 to 6,
2 wherein the peroxy compound is selected to
3 decompose at a temperature of the reservoir.
4
- 5 8. A method as claimed in any one of Claims 1 to 7,
6 wherein a co-additive may be optionally added to
7 the peroxy compound to either inhibit or
8 accelerate decomposition of the peroxy compound as
9 a function of temperature.
10
- 11 9. Use of a peroxy compound to inhibit bacterial
12 growth within a hydrocarbon reservoir.
13
- 14 10. Use of a peroxy compound to reduce the hydrogen
15 sulphide content of a hydrocarbon fluid.
16
- 17 11. Hydrocarbon fluid containing a peroxy compound or
18 a reactant thereof as an additive.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 97/01537

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C10G 27/12, A01N 37/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C10G, A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AU 53138/79 A1 (BIOLEX CORP.), 28 May 1981 (28.05.81), page 6, line 35 - page 8, line 1 - line 16, claims 1-7	1-11
	--	
A	EP 0082513 A1 (PEROXID-CHEMIE GMBH), 29 June 1983 (29.06.83)	1-11
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☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report			Publication date	Patent family member(s)		Publication date
AU	53138/79	A1	28/05/81	NONE		
EP	0082513	A1	29/06/83	CA	1205616 A	10/06/86
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				US	4548708 A	22/10/85